BIODEGRADATION OF MUSTARD AGENTS FROM ASSEMBLED CHEMICAL ROUNDS

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History Of Mustard Agent Biodegradation Studies At ECBC

- **1997: Harvey et.al., demonstrated that Sulfur Mustard (HD) could be neutralized in a simple hot water and caustic reaction. The main breakdown product in the HD hydrolysate, thiodiglycol could then be further degraded using a sequencing batch bioreactor with an activated sludge culture.**

- **1998: Guelta and DeFrank, demonstrated that HD hydrolysate could also be degraded using an immobilized cell bioreactor (ICB) at double the rate previously reported by Harvey.**

- **1999: Pilot-Scale demonstration study was completed using a 1000-gallon ICB to degrade a mixture of HD hydrolysate and a hydrolysate of tetrytol, the explosive in assembled chemical rounds stored at Pueblo Chemical Depot. Guelta et.al. 2001.**

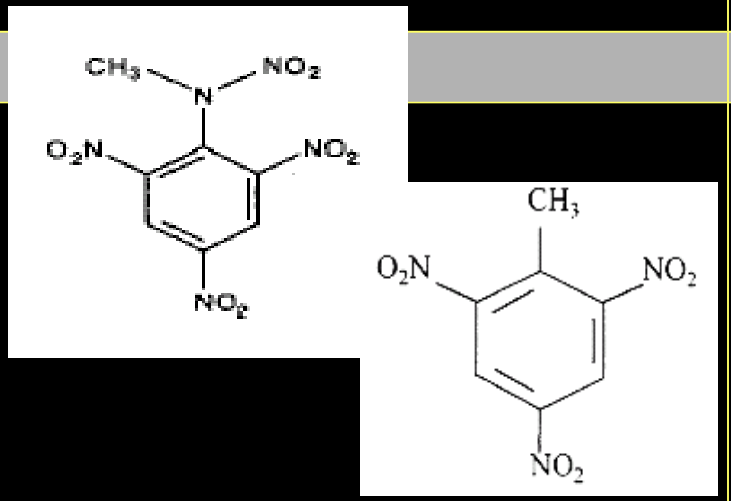
History Of Mustard Agent Biodegradation Studies At ECBC

- **2001: Pilot-Scale Engineering Design Study conducted for engineering design of a full-scale facility for PCD. This study included degradation of HD and Tetrytol hydrolysates at increased loadings, treatment of process condensate water, 3x rinse ate from dunnage operations and bioreactor effluent recycling. Guelta et.al.2001**

- **2002: Laboratory-Scale study degraded HD from Projectile Washout Studies (PWS) being conducted at Deseret Chemical Activity (DCA).**

- **2004: The current laboratory scale study evaluates the treatability of "HT" agent from projectile washout studies at DCA**

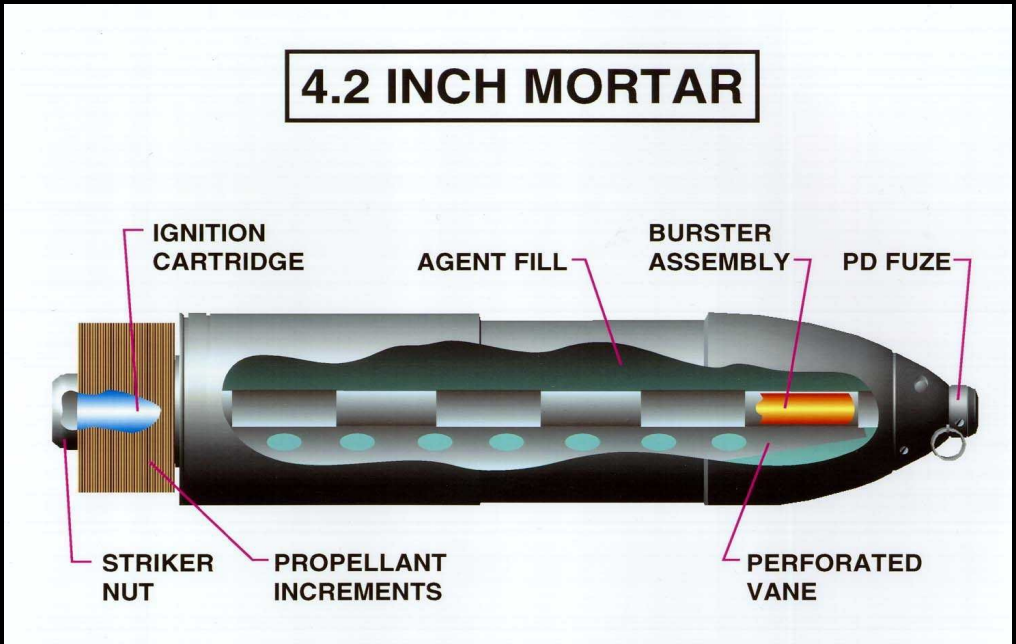
Agents Stored at PCD in Assembled Chemical

Component	Chemical Structure or Formula	Total Quantity (metric tons)
Agents		
HD **(distilled *b,b'*-dichloroethyl-sulfide, ~89% purity)**	$ClCH_2CH_2SCH_2CH_2Cl$	**2,350**
HT: ~67% HD ~22% T (bis 2-2-chlorethyl-thioethylether) ~ 11% impurities (i.e., other organo-sulfur compounds)	$ClCH_2CH_2SCH_2CH_2Cl$ (HD) $(ClCH_2CH_2SCH_2CH_2)_2O$ (T)	54
Explosives		
Tetrytol: mixture of ~70% tetryl (2,4,6-trinitrophenyl-methylnitramine) ~30% TNT (2,4,6-trinitrotoluene		101
Tetryl (2,4,6-trinitrophenyl-methylnitramine)	(see above)	

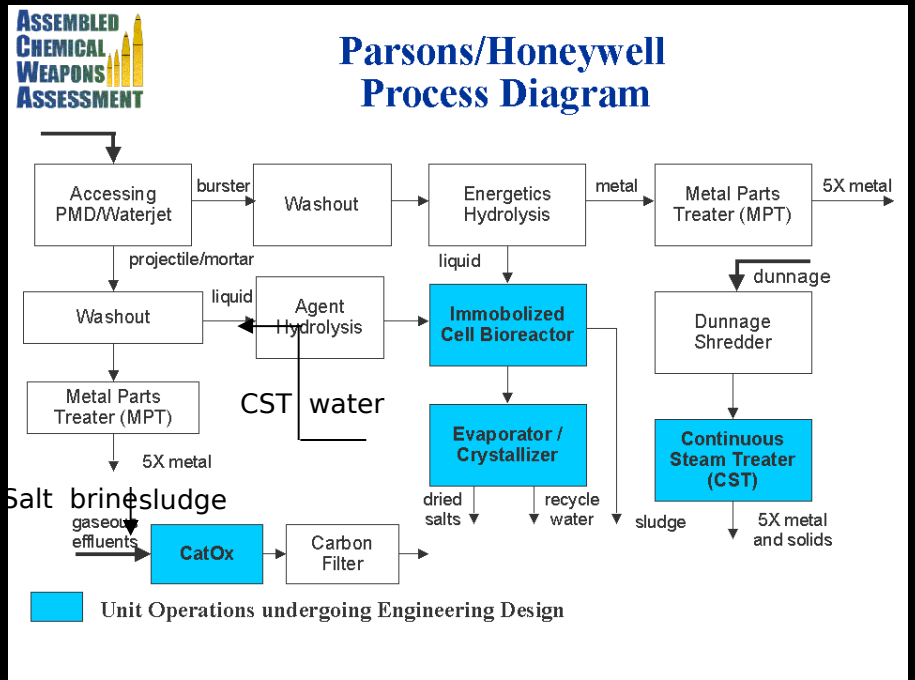
Energetics Stored at PCD

Propellants	Formula	Metric Tons
M1: mixture of **~84% nitrocellulose** **~9% dinitrotoluene** **~5% dibutylphthalate** **~1% diphenylamine** **~1% lead carbonate**	 $C_6H_{7.55}N_{2.45}O_{9.9}$ $C_7H_6N_2O_4$ $C_{16}H_{22}O_4$ $C_{12}H_{11}N$ CO_3Pb	**36**
M8: mixture of **~52% nitrocellulose** **~43% nitroglycerine** **~ 3% diethylphtalate** **~ 1% potassium nitrate** **~ 1% ethyl centralite**	 $C_6H_{7.55}N_{2.45}O_{9.9}$ $C_3H_5N_3O_9$ $C_{12}H_{14}O_4$ KNO_3 $C_{17}H_{20}N_2O$	**26**

Schematic of 4.2 Inch Chemical Round



Schematic of the Parsons/Honeywell Treatment Design



HT Treatability Scope and Objectives

Specific objectives of the test include:

- **Confirm the ability of the laboratory-scale ICBs to effectively treat the PWS-generated HT hydrolysate at hydraulic residence times (HRTs) that are representative of full-scale design by assessing the following parameters:**
- **Organic removal efficiency**
- **Elimination of thiodiglycol and other target organics in the HT hydrolysate**
- **Assess the impact of aluminum hydroxide in the energetics hydrolysate on ICB performance.**

Materials and Methods

HT Hydrolysate

- **HT hydrolysate was produced at Deseret Chemical Activity from 4.2-inch HT mortars**
- **Hydrolysate was produced at a nominal loading of 3.8 %**
- **Reaction period was 2 hours at 90°C**

Tetrytol Hydrolysate

- **Tetrytol Pellets were acquired from the Pantex Plant, TX**
- **Hydrolysate was produced with 6% caustic solution at 6.67 % (wt/vol) loading**
- **Reaction takes place at 90°C over 8-hour**

Major HT Hydrolysate Components

Component	HT Batch 11	HT Batch 12	HD
Thiodiglycol (TDG) (mg/L)	15,210	4,502	17,537
TOH (mg/L)	4,402	100	
QOH (mg/L)	1,189	454	
1,4-Thioxane (mg/L)	696.8	336.6	47.9
1,4-Dithiane (mg/L)	139.4	138.6	2,093
Chemical oxygen demand (COD), mg/L	51,800	15,200	43,100
Total organic carbon (TOC), mg/L	11,325	3,230	8,120
% TOC as TDG			84.9
COD:TOC ratio	4.57	4.71	5.31
Chloride (mg/L)	8,490	1,020	10,800
Sulfate (mg/L)	42	38	84
Sulfur (mg/L)			6,010
Sodium (mg/L)	11,000	8,400	10,630
pH, pH units	12.82	13.31	13.0

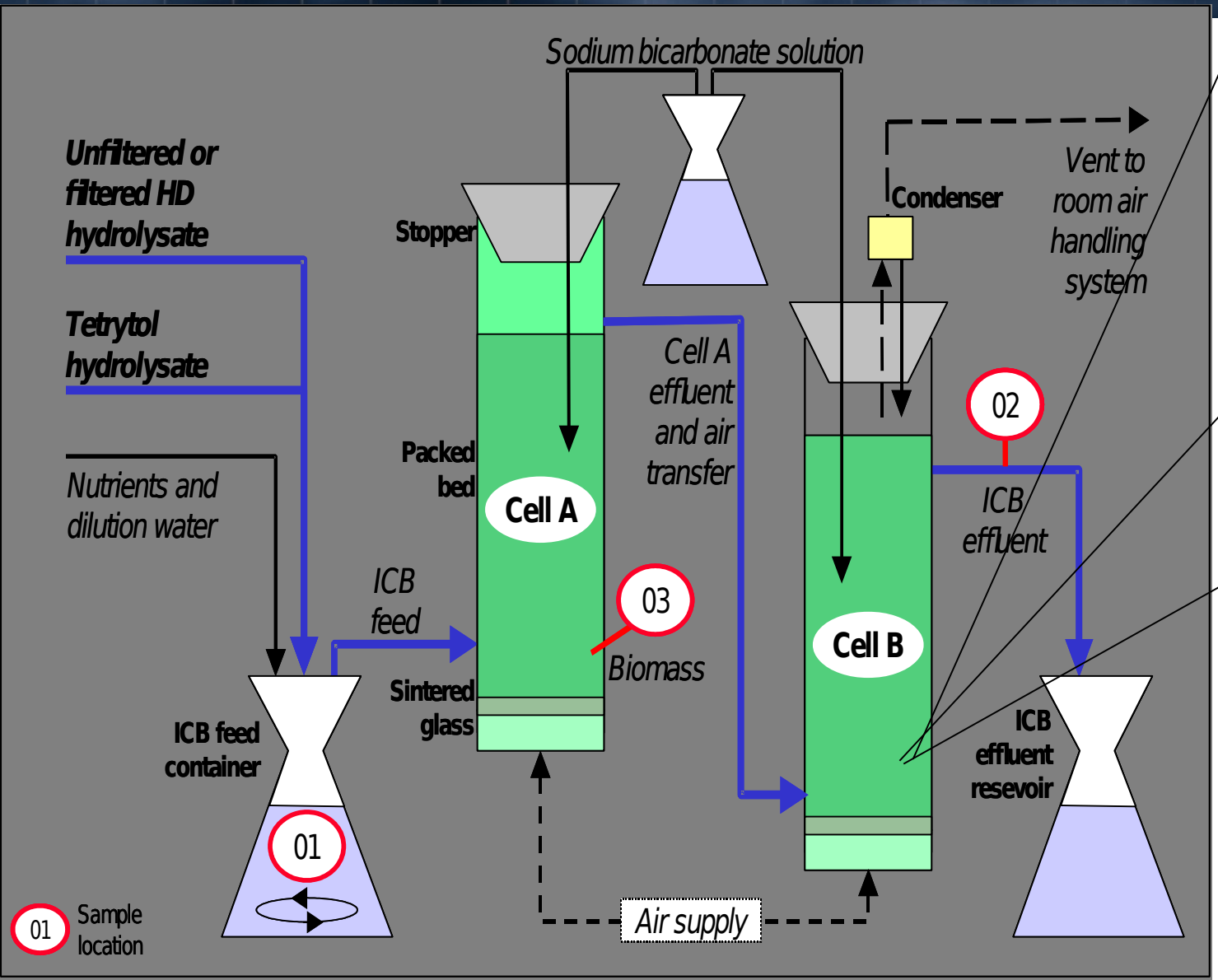
TOH= 1,2-bis (hydroxyethylthio) ethane, QOH= 1,2-bis(2-hydroxyethylthio) ethyl ether

Typical ICB Feed Recipes

Item	Batch 11	Batch 12	Unit
HD hydrolysate (3.8 wt%)	300	975	mL
Tetrytol hydrolysate (6.67 wt/vol%)	15	15	mL
NH_4Cl	1.25	1.25	G
Potassium Phosphate Di-basic (K_2HPO_3)	0.25	0.25	G
Sulfur-free Wolin Salts	10	10	mL
HCl		17	mL
Tap water to volume	~685	0	mL
Final volume	1000	~1000	mL

- **A 1.2-Liter ICB system was used to study the biotreatability of "HT" and HT with Aluminum Hydroxide.**
- **Reactors are inoculated with activated sludge received from a local municipal waste water treatment plant.**

Schematic of Laboratory-Scale ICB Reactors



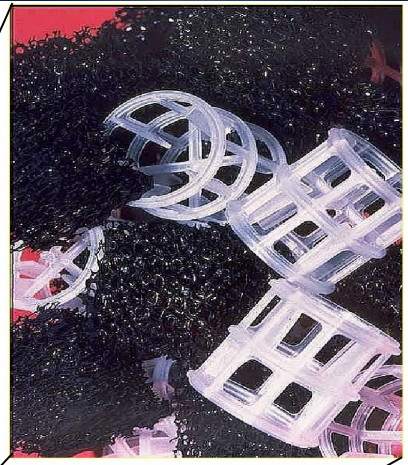
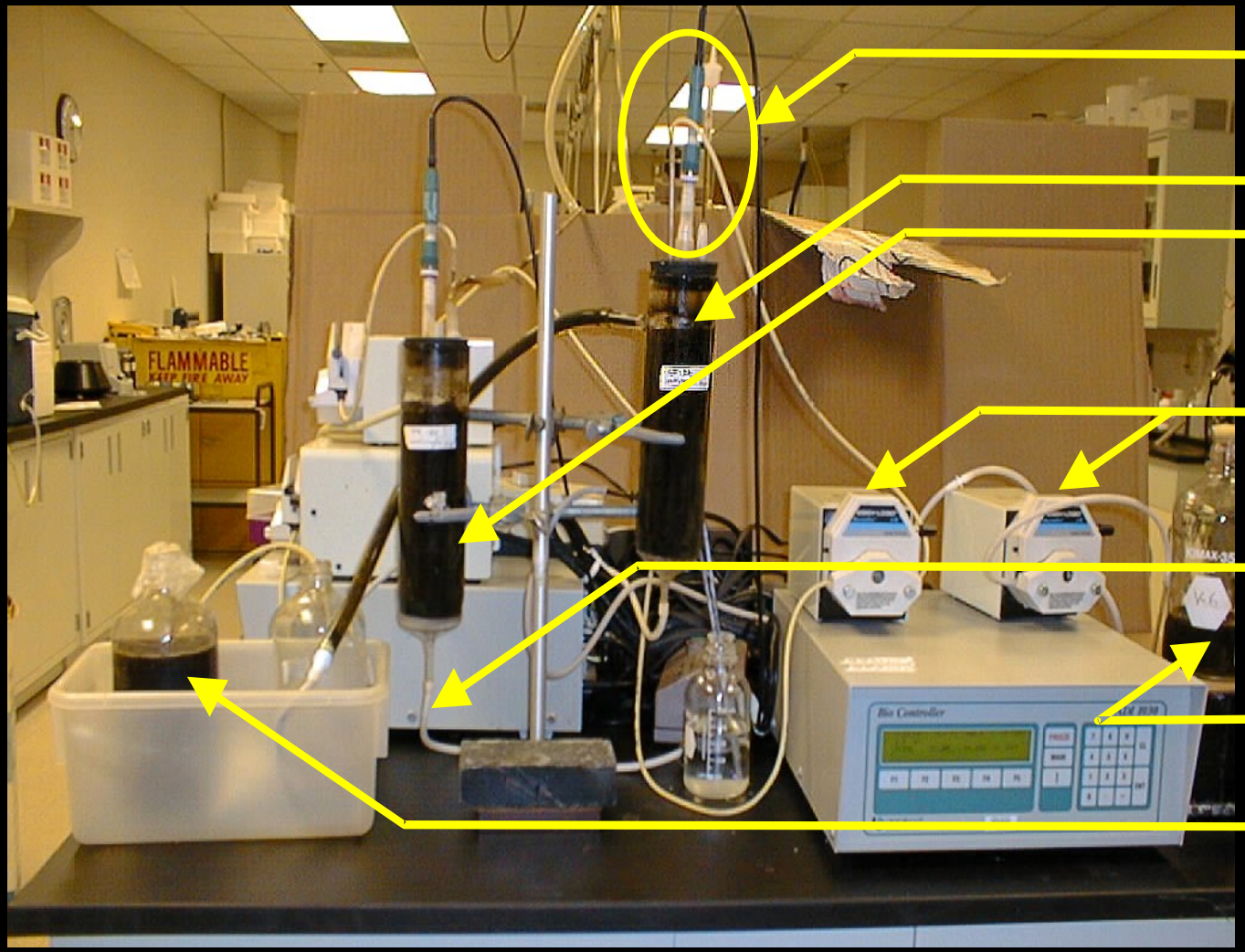


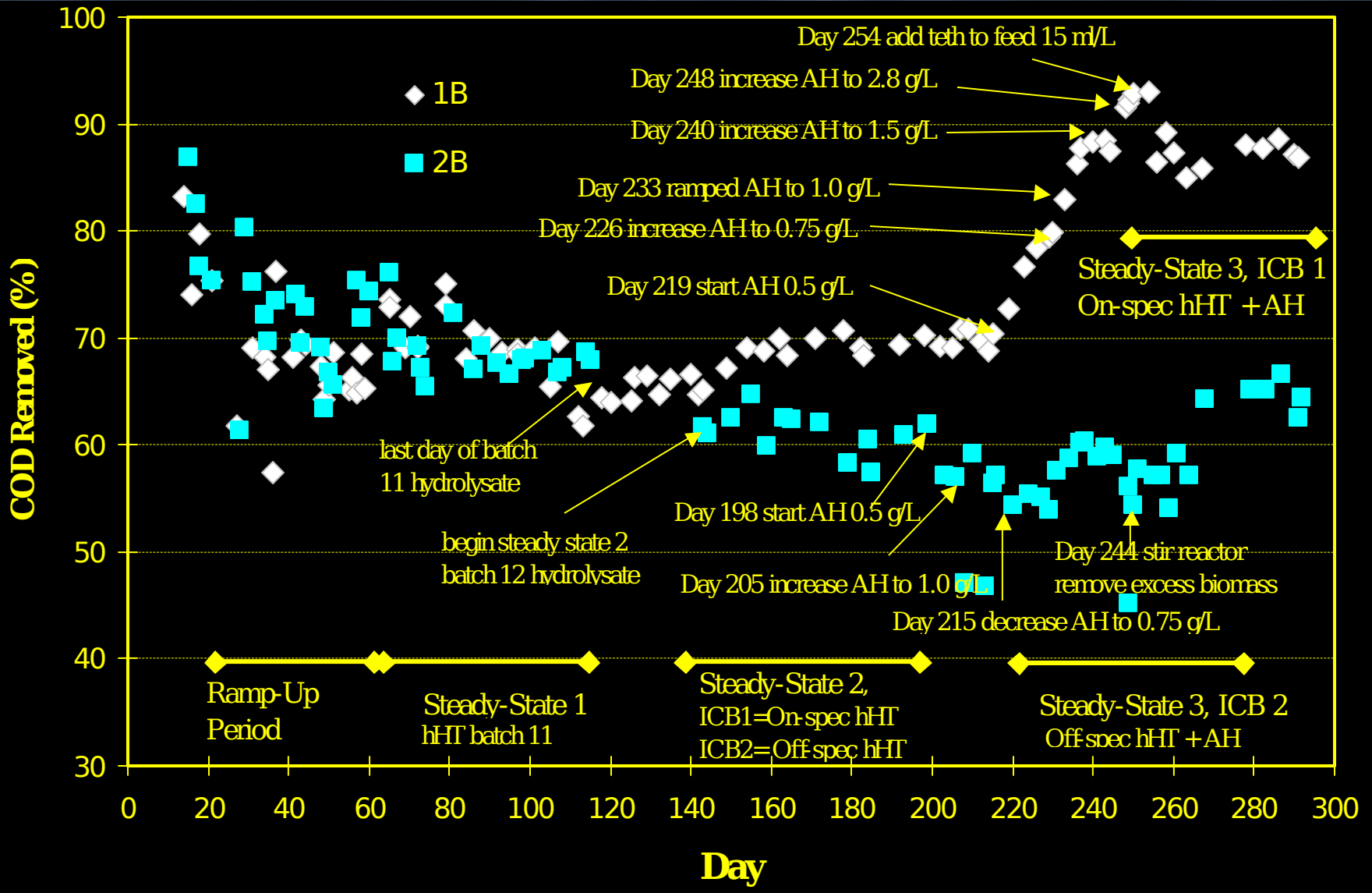
Photo of Laboratory-Scale ICB's



Phases of HT Study Plan

Test Phase	ICB-1	ICB-2
Phase 1 60-days	Comparative testing of on-spec hHT batch 11	hHT batch 11
Phase 2 60-days	Batch 11 hHT, control for hHT batch 12	Off-spec hHT batch 12
Phase 3	Addition of Aluminum	Addition of Aluminum

COD Removal Efficiency Across ICB's During Study



Comparison of ICB COD Removal and Breakdown Products Removal for 3 Steady-State Periods.

	ICB 1			ICB 2		
Steady State #	COD Feed (mg/L)	COD Effluent (mg/L)	COD % Removed	COD Feed (mg/L)	COD Output Efluent (mg/L)	COD % Removed
1	17221	5748	67	16710	5459	67
2	16711	5402	68	15236	5794	62
3	16438	3644	78	15484	6511	58

ICB1

Steady State #	TDG (mg/L) input/output	1,4-Dithane (mg/L) input/output	QOH (mg/L) input/output	TOH (mg/L) input/output	1,4-thioxane (mg/L) input/output
1	4921 / <1	114 / 19	401 / <1	1689 / <2	317 / 9
2	4837 / <1	122 / <2	379 / <2	1682 / <2	330 / 18
3	4933 / <1	133 / <2	380 / <2	1751 / <2	358 / 13

ICB 2

Steady State #	TDG (mg/L) input/output	1,4-Dithane (mg/L) input/output	QOH (mg/L) input/output	TOH (mg/L) input/output	1,4-thioxane (mg/L) input/output
1	4879 / <1	116 / <1	388 / <1	1740 / <2	324 / 14
2	4312 / <2	118 / <2	243 / <2	1675 / <2	256 / 10
3	NA	NA	NA	NA	NA

"<" indicates detection limit for sample, chemical of interest non-detect

Summary of Comparative Performance Between Lab and Pilot-Scale Studies Conducted Using HD/HT Agent from Ton Containers Versus Chemical Rounds.

Data is normalized to I

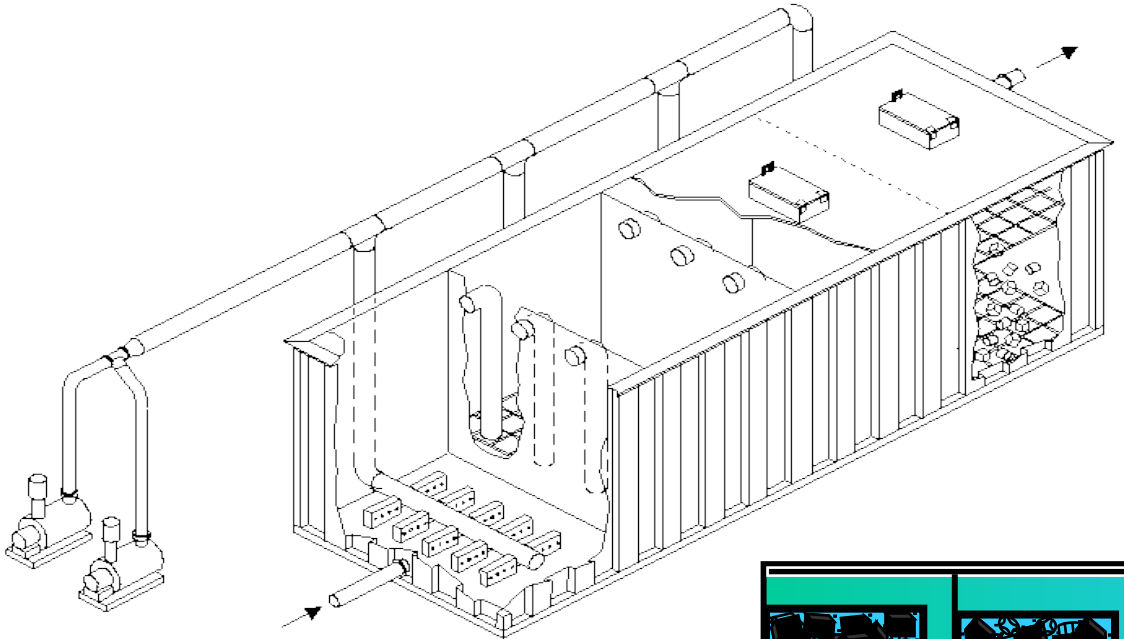
- **Pilot-Scale, HD from Ton Containers**
- **Lab-Scale, HD/HT From PCD Chemical Rounds**

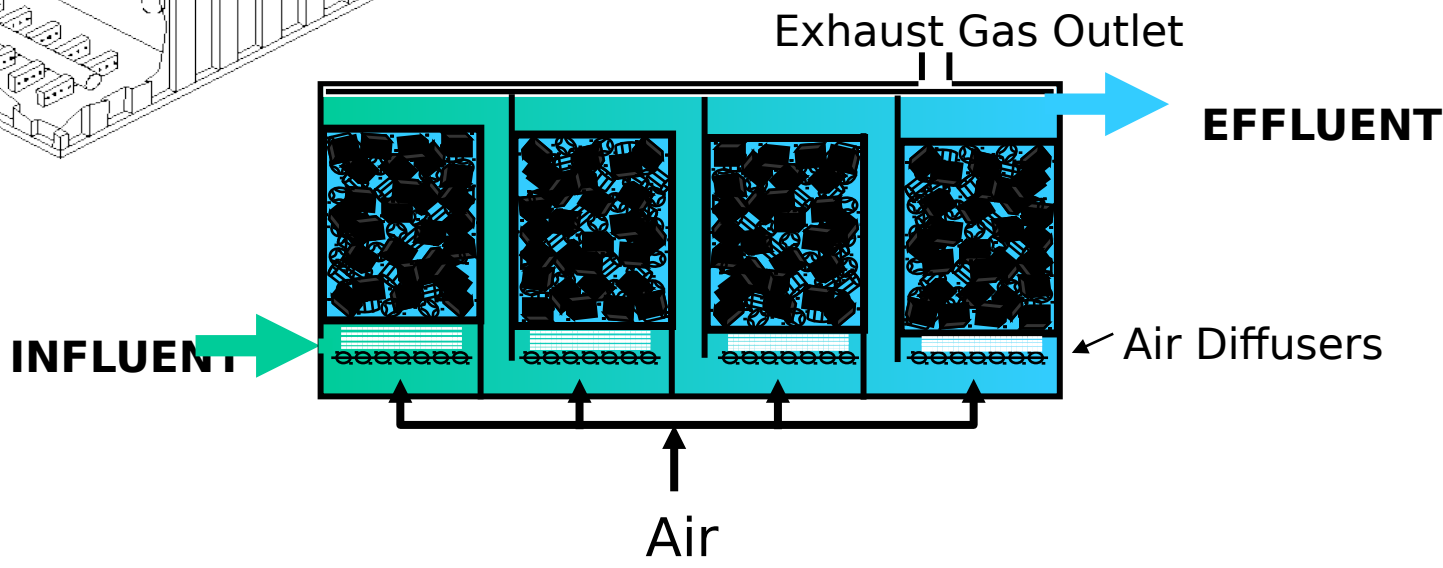
1999
2001
2002
2004

Test ICB	COD Input (mg/Day/L)	COD Output (mg/Day L)	% COD Removal Efficiency	TDG Input (mg/Day/L)	TDG Consumption (mg/Day/L)
Demo I Pilot ICB	1298	115	91.1	612	612
EDS Pilot ICB	2266	217	90.4	1069	1069
PWS ICB 1 unfiltered hHD	2375	349	85.5	1141	1128
PWS ICB 2 filtered hHD	2411	350	85.6	1092	1084
PWS HT-ICB-1	3512	817	74	1021	1020.7
PWS HT ICB-2	3162	1067	60	945.7	945.66

Degradation of organics from chemical rounds is more difficult than from ton containers. Organics from HT rounds more difficult to degrade than from HD. Source seems to have no effect on the biodegradation of the Mustard principal breakdown product TDG.

Honeywell ICB Design





The full-scale treatment facility under construction at Pueblo Chemical Depot, CO. will employ 24 40-thousand gallon ICB's similar to the Honeywell systems below.

Approximate PCD Capacity

(40,000 / 5-day hrt) x 1% HD ≃ 80 gal/Day/ICB

80 gal/Day/ICB x 24 ICB's ≃ 1920 gal/day HD

Two 40-thousand gallon ICB's (Honeywell)

Transition and Further Studies

As of this writing this program is being transitioned to Bectel/Battelle for further engineering design and process development. Laboratory studies will continue at Battelle, Aberdeen MD.

Further studies in the area have continued with a laboratory study to evaluate the potential for the advanced oxidation and biodegradation of solid propellants associated with the chemical agent and non-stockpile items.